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THERMODYNAMICS OF SOLUTIONS OF ETHANOL IN NONASSOCIATING COMPONENTS *

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ABSTRACT

The spectroscopic and thermodynamic properties of solutions of ethanol in nonassociating components can be described with good accuracy by the associated solution model of Nagata and Tamura (1982) based on mole fraction statistics.

LIST OF SYMBOLS

A, B	alcohol and nonassociating component
C_i, D_i	constants of eqn. (27)
G_{ij}	coefficient as defined by $\exp(-\alpha_{ij}\tau_{ij})$
g	excess Gibbs free energy
g_{ij}	binary interaction parameter
h_2	enthalpy of formation of dimer
h_A	enthalpy of hydrogen bond formation in i-mer
h_{AB}	enthalpy of formation of chemical complex A_iB
h^E	excess enthalpy
K_2	equilibrium constant of dimer formation
K_3	equilibrium constant of open chain trimer formation
K	equilibrium constant of open chain i-mer formation, $i > 3$
K_{cy}	equilibrium constant for cyclization of open chain i-mer as defined by θ/i, $i > 4$
K_{AB}	equilibrium constant of formation of chemical complex A_iB
P	total pressure
P_i^s	saturated vapor pressure of pure component i
R	gas constant

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S	stoichiometric sum
T	absolute temperature
v_i^L	molar liquid volume of pure component i
x_i	liquid phase mole fraction of component i
y_i	vapor phase mole fraction of component i
z	coefficient as defined by Kx_{A_1}

Greek letters

α_{ij}	nonrandomness parameters of NRTL equation
β	coefficient as defined by eqn. (28)
γ_i	activity coefficient of component i
θ	constant related to K_{cy}
μ	chemical potential
τ_{ji}	coefficient as defined by $(g_{ji}-g_{ii})/RT$
ϕ_i	vapor phase fugacity coefficient of component i
ϕ_i^s	vapor phase fugacity coefficient of pure component i at system temperature T and pressure P_i^s

Subscripts

A, B	alcohol and nonassociating component
A_1, A_i	alcohol monomer and i-mer
A_iB	complex formation between alcohol i-mer and component B
chem	chemical
phys	physical
1, 2	alcohol and nonassociating component

Superscripts

E	excess
L	liquid
s	saturation
*	pure alcohol

INTRODUCTION

Stokes' chemical model [1] can reproduce well the spectroscopic and dielectric properties and the inflexions found in the partial thermodynamic properties of dilute solutions of ethanol in cyclohexane. The same model, with the addition of a solvation equilibrium, is able to account satisfactorily for the thermodynamic properties of ethanol in *p*-xylene [2]. The model works only at the dilute concentration range of ethanol. To cover the whole composition range, an improved model was developed [3], based on that of

Stokes [1], which has been used to correlate isothermal phase equilibrium data and excess enthalpy data of binary solutions of methanol and a solvating component and to predict phase equilibrium and excess enthalpy data of ternary solutions of methanol and solvating components. In this paper the new model is extended to the spectroscopic and thermodynamic properties of solutions of ethanol in nonassociating components.

ASSOCIATION MODEL

The model is similar to that previously used by Stokes, except that the NRTL equation [4] is used in place of the physical interaction term. To give a quantitative reproduction of the activity coefficients, excess enthalpies, and infrared spectroscopic behavior and to account for the initial decrease in the apparent dipole moment, the following was selected for the model in accordance with Stokes' assumptions.

(1) Open chains of any length are present according to stepwise reactions and three equilibrium constants, K_2, K_3 and K, are defined respectively as follows

$$\mathrm{A} + \mathrm{A} = \mathrm{A}_2 \qquad K_2 = x_{\mathrm{A}_2}/x_{\mathrm{A}_1}^2 \tag{1}$$

$$\mathrm{A}_2 + \mathrm{A} = \mathrm{A}_3 \qquad K_3 = x_{\mathrm{A}_3}/x_{\mathrm{A}_2}x_{\mathrm{A}_1} \tag{2}$$

$$\mathrm{A}_i + \mathrm{A} = \mathrm{A}_{i+1} \qquad K = x_{\mathrm{A}_{i+1}}/x_{\mathrm{A}_i}x_{\mathrm{A}_1} \text{ for all } i \geqslant 3 \tag{3}$$

(2) Closed cyclic groups are also present and the first cyclic species is a pentamer. The cyclic groups are in equilibrium with the open chains of the same number of members and the equilibrium constant has the form

$$\mathrm{A}_i(\text{linear}) = \mathrm{A}_i(\text{cyclic}) \quad K_{\mathrm{cy}} = \theta/i = x_{\mathrm{A}_i(\text{cyclic})}/x_{\mathrm{A}_i(\text{linear})} \text{ for all } i > 4 \tag{4}$$

where θ is independent of i.
For the ethanol–solvating component systems, the model should include a solvation equilibrium between the terminal hydroxyl group of polymeric alcohol species and one solvating molecule (B).

$$\mathrm{A}_i(\text{linear}) + \mathrm{B} = \mathrm{A}_i\mathrm{B} \quad K_{\mathrm{AB}} = x_{\mathrm{A}_i\mathrm{B}}/x_{\mathrm{A}_i}x_{\mathrm{B}_1} \text{ for all } i \geqslant 1 \tag{5}$$

The value of K_2K_3/K^2 has to be independent of temperature according to the model. The temperature dependence of K_2, K_3, K, θ and K_{AB} should be given by, respectively

$$\begin{aligned} &\partial \ln K_2/\partial(1/T) = -h_2/R, && \partial \ln K_3/\partial(1/T) = -(2h_{\mathrm{A}} - h_2)/R \\ &\partial \ln K/\partial(1/T) = -h_{\mathrm{A}}/R, && \partial \ln \theta/\partial(1/T) = -h_{\mathrm{A}}/R \\ &\partial \ln K_{\mathrm{AB}}/\partial(1/T) = -h_{\mathrm{AB}}/R \end{aligned} \tag{6}$$

The chemical potential of the stoichiometric species is equal to that of the monomeric one [5].

$$\mu_A = \mu_{A_1}, \mu_B = \mu_{B_1} \tag{7}$$

Then, the chemical contribution terms of the excess Gibbs energy and activity coefficients for the ethanol (1)–solvating component (2) system are expressed by

$$g^E_{chem}/RT = x_1 \ln(x_{A_1}/x^*_{A_1}x_1) + x_2 \ln(x_{B_1}/x_2) \tag{8}$$

$$(\ln \gamma_1)_{chem} = \ln(x_{A_1}/x^*_{A_1}x_1) \tag{9}$$

$$(\ln \gamma_2)_{chem} = \ln(x_{B_1}/x_2) \tag{10}$$

The true mole fractions of the monomeric species, x_{A_1} and x_{B_1}, are related to the stoichiometric mole fraction x_1

$$\begin{aligned} x_1 = \Big\{&(1 + K_{AB}x_{B_1})\left[x_{A_1} + 2K_2x^2_{A_1} + K_2K_3(3-2z)x^3_{A_1}/(1-z)^2\right] \\ &+K_2K_3K^2\theta x^5_{A_1}/(1-z)\Big\}/S \end{aligned} \tag{11}$$

where $z = Kx_{A_1}$ and S is the stoichiometric sum given by

$$\begin{aligned} S = &(1 + K_{AB}x_{B_1})\left[x_{A_1} + 2K_2x^2_{A_1} + K_2K_3(3-2z)x^3_{A_1}/(1-z)^2\right] \\ &+K_2K_3K^2\theta x^5_{A_1}/(1-z) \\ &+K_{AB}x_{B_1}\left[x_{A_1} + K_2x^2_{A_1} + K_2K_3x^3_{A_1}/(1-z)\right] + x_{B_1} \end{aligned} \tag{12}$$

The sum of the mole fractions of all chemical species present in the solution must be unity

$$\begin{aligned} &(1 + K_{AB}x_{B_1})\left[x_{A_1} + K_2x^2_{A_1} + K_2K_3x^3_{A_1}/(1-z)\right] \\ &-(K_2K_3\theta/K^3)\left[\ln(1-z) + z + z^2/2 + z^3/3 + z^4/4\right] + x_{B_1} = 1 \end{aligned} \tag{13}$$

The value of $x^*_{A_1}$ is obtained from eqn. (14) at pure alcohol state

$$\begin{aligned} &\left[x^*_{A_1} + K_2x^{*2}_{A_1} + K_2K_3x^{*3}_{A_1}/(1-z^*)\right] \\ &-(K_2K_3\theta/K^3)\left[\ln(1-z^*) + z^* + z^{*2}/2 + z^{*3}/3 + z^{*4}/4\right] = 1 \end{aligned} \tag{14}$$

For the physical contribution term the NRTL equation is adopted [4], though Stokes used the Scatchard–Hildebrand equation

$$g^E_{phys}/RT = x_1x_2\left[\tau_{21}G_{21}/(x_1 + x_2G_{21}) + \tau_{12}G_{12}/(x_2 + x_1G_{12})\right] \tag{15}$$

$$(\ln \gamma_1)_{phys} = x_2^2\left[\tau_{21}G^2_{21}/(x_1 + x_2G_{21})^2 + \tau_{12}G_{12}/(x_2 + x_1G_{12})^2\right] \tag{16}$$

$$(\ln \gamma_2)_{phys} = x_1^2\left[\tau_{12}G^2_{12}/(x_2 + x_1G_{12})^2 + \tau_{21}G_{21}/(x_1 + x_2G_{21})^2\right] \tag{17}$$

where

$$\tau_{21} = (g_{21} - g_{11})/RT \qquad \tau_{12} = (g_{12} - g_{22})/RT \tag{18}$$

$$G_{21} = \exp(-\alpha_{21}\tau_{21}) \qquad G_{12} = \exp(-\alpha_{12}\tau_{12}) \tag{19}$$

Finally the excess Gibbs free energy and activity coefficients are given by the sum of both contributions

$$g^{\mathrm{E}} = g^{\mathrm{E}}_{\mathrm{chem}} + g^{\mathrm{E}}_{\mathrm{phys}} \tag{20}$$

$$\ln \gamma_1 = (\ln \gamma_1)_{\mathrm{chem}} + (\ln \gamma_1)_{\mathrm{phys}} \tag{21}$$

$$\ln \gamma_2 = (\ln \gamma_2)_{\mathrm{chem}} + (\ln \gamma_2)_{\mathrm{phys}} \tag{22}$$

The excess enthalpy of the solution is obtained by the sum of the chemical and physical contributions terms similarly

$$h^{\mathrm{E}} = h^{\mathrm{E}}_{\mathrm{chem}} + h^{\mathrm{E}}_{\mathrm{phys}} \tag{23}$$

$$\begin{aligned} h^{\mathrm{E}}_{\mathrm{chem}} = {} & \Big\{(1 + K_{\mathrm{AB}}x_{\mathrm{B}_1})\Big[h_2K_2x^2_{\mathrm{A}_1} + h_{\mathrm{A}}K_2K_3x^3_{\mathrm{A}_1}(2 - z)/(1 - z)^2\Big] \\ & + h_{\mathrm{A}}K_2K_3K^2\theta x^5_{\mathrm{A}_1}/(1 - z) \\ & + h_{\mathrm{AB}}K_{\mathrm{AB}}x_{\mathrm{B}_1}\Big[x_{\mathrm{A}_1} + K_2x^2_{\mathrm{A}_1} + K_2K_3x^3_{\mathrm{A}_1}/(1 - z)\Big]\Big\}/S \\ & - x_1\Big[h_2K_2x^{*2}_{\mathrm{A}_1} + h_{\mathrm{A}}K_2K_3x^{*3}_{\mathrm{A}_1}(2 - z^*)/(1 - z^*)^2 \\ & + h_{\mathrm{A}}K_2K_3K^2\theta x^{*5}_{\mathrm{A}_1}/(1 - z^*)\Big]/S^* \end{aligned} \tag{24}$$

$$\begin{aligned} h^{\mathrm{E}}_{\mathrm{phys}} = \frac{\partial\left(g^{\mathrm{E}}_{\mathrm{phys}}/T\right)}{\partial(1/T)} = {} & Rx_1x_2\left\{\frac{\tau'_{21}G_{21}}{x_1 + x_2G_{21}} + \frac{\tau'_{12}G_{12}}{x_2 + x_1G_{12}}\right. \\ & \left. - \alpha_{12}\left[\frac{x_1\tau_{21}G_{21}\tau'_{21}}{(x_1 + x_2G_{21})^2} + \frac{x_2\tau_{12}G_{12}\tau'_{12}}{(x_2 + x_1G_{12})^2}\right]\right\} \end{aligned} \tag{25}$$

where S^* is the value of S at pure alcohol state and

$$\tau'_{21} = \partial\tau_{21}/\partial(1/T) \qquad \tau'_{12} = \partial\tau_{12}/\partial(1/T) \tag{26}$$

The energy parameters are assumed to vary linearly with temperature

$$g_{21} - g_{11} = C_1 + D_1(T - 273.15) \qquad g_{12} - g_{22} = C_2 + D_2(T - 273.15) \tag{27}$$

The infrared spectroscopic results furnish the ratio of the number of free hydroxyl groups to the stoichiometric number of alcohol molecules, β

$$\beta = \frac{\sum_{i=1}^{\infty} x_{A_i(\mathrm{linear})}}{\sum_{i=1}^{\infty} i x_{A_i(\mathrm{linear})} + \sum_{i=5}^{\infty} i x_{A_i(\mathrm{cyclic})}}$$

$$= \frac{x_{A_1} + K_2 x_{A_1}^2 + K_2 K_3 x_{A_1}^3/(1-z)}{x_{A_1} + 2K_2 x_{A_1}^2 + \left(K_2 K_3/K^3\right) z^3\left[(3-2z)/(1-z)^2 + \theta z^2/(1-z)\right]} \tag{28}$$

REPRESENTATION OF BINARY EXPERIMENTAL DATA

We use four equilibrium constants at 25°C and two enthalpies of hydrogen-bond formation for ethanol: $K_2 = 40$, $K_3 = 110$, $K = 45$ and $\theta = 85$; $h_2 = -21.2$ kJ mol^{-1} and $h_A = -23.5$ kJ mol^{-1}. The values of h_2 and h_A are assumed to be temperature-independent. The values of the equilibrium constants are not the same as those given by Stokes [1]. It was found that the new model with a set of the equilibrium constants recommended by Stokes was unable to represent adequately the thermodynamic functions of the system ethanol–cyclohexane over the entire range of concentration. After many trials to find a best set of the equilibrium constants, the new values of the equilibrium constants are selected which reproduce well the spectroscopic data as well as the thermodynamic functions for the system ethanol–cyclohexane over the whole composition range. Table 1 lists the values of the solvation equilibrium constants and their enthalpies of complex formation used in data reduction. The enthalpies of complex formation were estimated by taking the difference between the value of enthalpy of dilution of ethanol in cyclohexane and that in a solvating component at 25°C as

TABLE 1

Solvation equilibrium constants at 25°C and enthalpies of complex formation

System	K_{AB}	h_{AB} (kJ mol^{-1})
Ethanol–benzene	3.6	−8.2
Ethanol–chloroform	20	−24.5
Ethanol–ethyl acetate	15	−15
Ethanol–2-butanone	20	
Ethanol–tetrachloromethane	1.4	−5.5
Ethanol–toluene	3.3	−8.3
Ethanol–*p*-xylene	3.2	−8.3

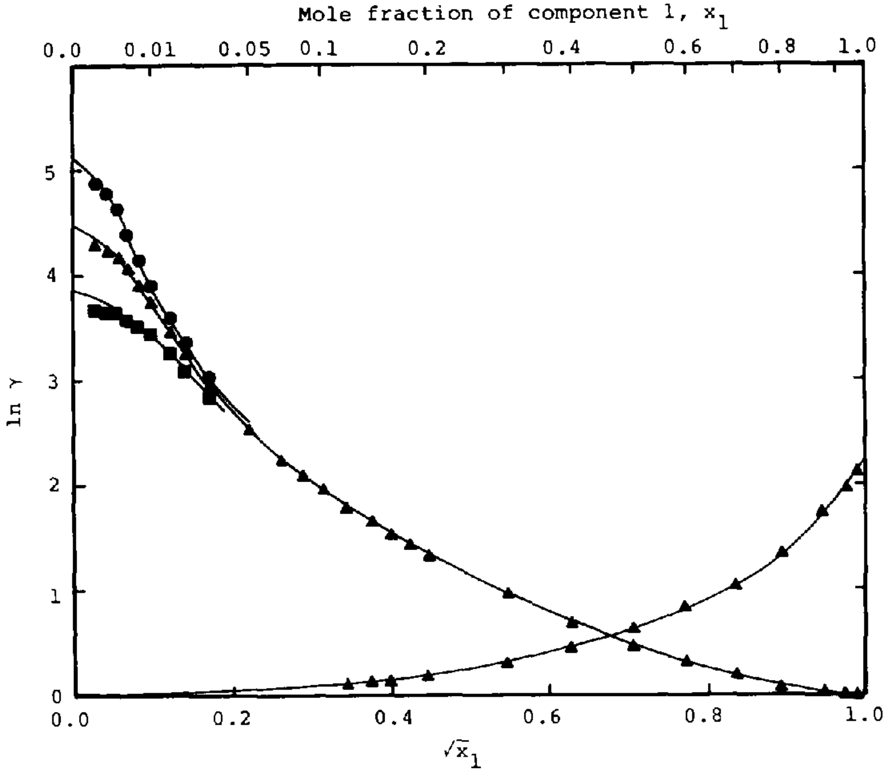


Fig. 1. Activity coefficients for ethanol(1)–cyclohexane(2). Calculated (————). Experimental (●, 6.7°C; ▲, 25°C; ■, 45°C), data of Stokes and Adamson [6]. Experimental data at 6.7 and 45°C are shown at only very diluted concentrations of ethanol.

TABLE 2

Results of g^E/x_1x_2 and h^E/x_1x_2 data reduction

Data type	Temp (°C)	No. of data points	Abs. arith. mean dev. (J mol^{-1})	C_1 (J mol^{-1})	C_2 (J mol^{-1})	D_1 (J mol^{-1} K^{-1})	D_2 (J mol^{-1} K^{-1})	Ref.
Ethanol(1) – cyclohexane(2)								
g^E	6.73	27	3.8	1494.00	−401.61			6
	25	27	6.7	1393.41	−349.98			
	45	27	8.6	1265.67	−277.01			
h^E	6.73	27	6.7	14510.3	2222.64	48.1765	0.9087	6
	25	27	5.8	19737.0	699.41	67.1318	−2.7936	
	45	27	8.5	15606.0	410.03	50.5292	−2.1372	
Ethanol(1) – p-xylene(2)								
g^E	13.3	25	5.1	1098.03	−123.26			2
	25	25	4.7	755.17	285.30			
	35	25	4.6	440.49	692.40			
	45	25	4.3	199.91	1055.69			
h^E	13.3	25	10.1	17387.1	4513.35	62.8685	28.0306	2
	25	25	10.9	15112.4	4352.67	54.1560	28.5440	
	35	25	10.9	13169.7	4120.16	46.6960	28.3680	
	45	25	11.6	10601.3	3990.50	36.7524	28.4505	

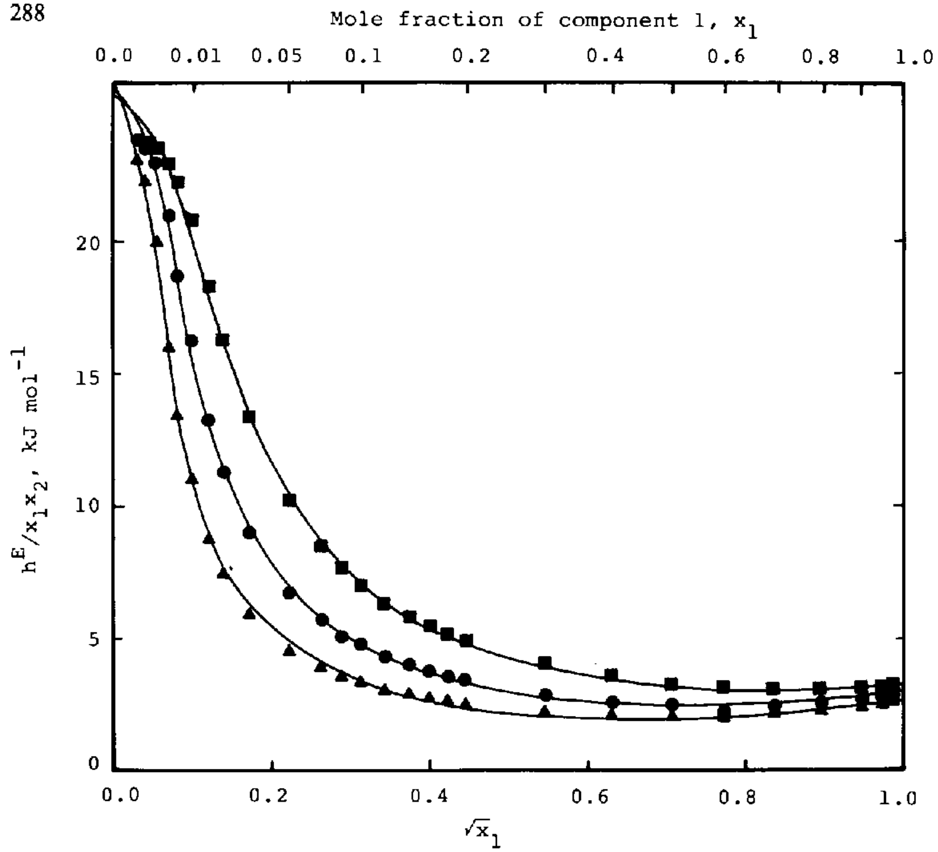


Fig. 2. Molar excess enthalpies of ethanol(1)-cyclohexane(2). Calculated (————). Experimental (▲, 6.7°C; ●, 25°C; ■, 45°C), data of Stokes and Adamson [6].

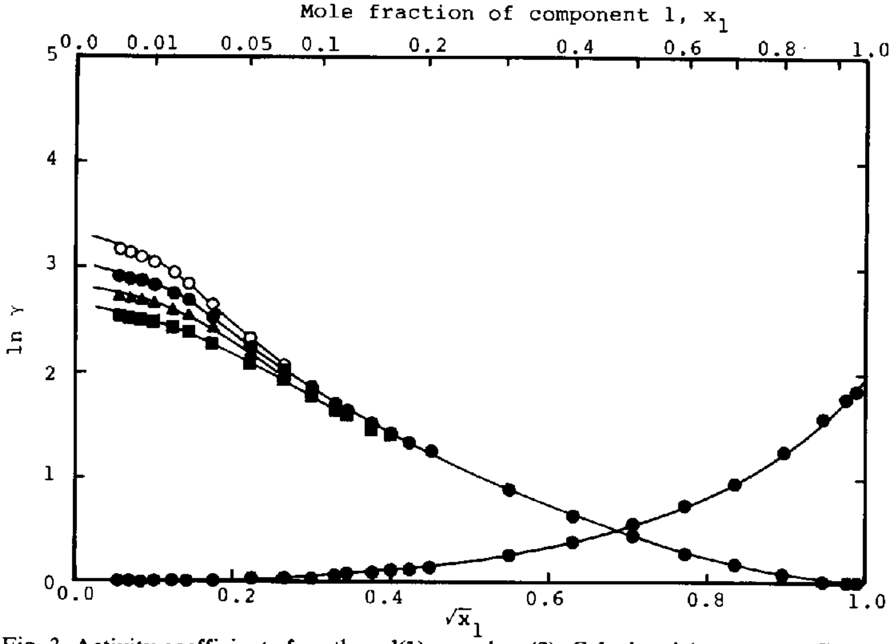


Fig. 3. Activity coefficients for ethanol(1)–*p*-xylene(2). Calculated (————). Experimental (○, 13.3°C; ●, 25°C; ▲, 35°C; ■, 45°C), data of Stokes and French [2]. Experimental data at 13.3, 35 and 45°C are shown at only very diluted concentrations of ethanol.

TABLE 3

Results of vapor–liquid equilibrium data reduction

System (1–2)	Temp. (°C)	No. of data points	C_1 (J mol^{-1})	C_2 (J mol^{-1})	Abs. arith. mean dev.		Ref.
					Vapor mole fraction ($\times 10^3$)	Pressure (mm Hg)	
Ethanol–benzene	25	11	4090.33	−2204.83	7.3	0.5	12
	50	5	764.65	264.65	9.8	4.0	13
Ethanol–chloroform	35	15	6161.62	−2939.45	8.0	1.9	14
Ethanol–cyclohexane	50	5	978.76	108.15	4.2	1.3	15
Ethanol–*n*-hexane	35	9	1896.48	−597.66	7.2	2.4	16
Ethanol–2-butanone	25	12	−1137.94	1624.51	9.7	0.9	12
Ethanol–tetrachloromethane	45	13	4482.42	−2559.08	7.3	2.8	17
	65	15	4052.00	−2231.32	5.5	3.9	
Ethanol–toluene	50	5	997.07	76.42	3.8	1.1	15
Benzene–cyclohexane	50	5	2138.02	−502.08	7.2	1.1	13
Chloroform–*n*-hexane	35	9	−884.40	2676.88	3.2	0.9	16
2-Butanone–benzene	25	10	4414.41	−2501.95	5.6	1.1	12
Toluene–cyclohexane	50	5	836.80	83.68	4.0	1.0	15

TABLE 4

Results of excess enthalpy data reduction

System (1–2)	Temp. (°C)	No. of data points	Abs. arith. mean dev. ($J mol^{-1}$)	C_1 ($J mol^{-1}$)	C_2 ($J mol^{-1}$)	D_1 ($J mol^{-1} K^{-1}$)	D_2 ($J mol^{-1} K^{-1}$)	Ref.
Ethanol–benzene	25	10	1.7	120.96	6986.55	4.6172	37.8916	18
Ethanol–chloroform	25	29	17.9	7986.24	4817.31	1.1679	38.6312	19
Ethanol–cyclohexane	25	21	0.8	6904.29	2622.38	24.1327	4.4041	20
Ethanol–ethyl acetate	25	13	6.0	8382.00	3024.86	35.5601	12.9677	21
Ethanol–tetrachloromethane	35	14	7.7	5993.65	4581.52	29.7800	36.4454	22
Ethanol–toluene	25	10	1.8	4462.02	5281.62	19.8420	32.9334	18
Ethanol–*p*-xylene	25	16	6.9	7909.29	4248.70	31.4175	27.5858	23
Benzene–cyclohexane	25	23	2.2	−387.62	−4879.50	−11.8441	−18.1458	20
Ethyl acetate–cyclohexane	25	15	5.7	3064.03	4049.85	−11.4516	5.5445	24
Toluene–cyclohexane	25	12	3.3	1127.62	−1034.15	−13.0536	1.7853	25
p-Xylene–cyclohexane	25	19	2.6	1609.44	−956.63	−11.8524	2.6662	23

TABLE 5

Predicted results for ternary vapor–liquid equilibria

System	Temp. (°C)	No. of data points	Abs. arith. mean dev.		Ref.
			Vapor mole fraction (×1000)	Pressure (mm Hg)	
Ethanol–benzene–cyclohexane	50	19	10.6 4.8 8.4	7.2	13
Ethanol–toluene–cyclohexane	50	19	7.3 4.5 5.2	3.4	15
Ethanol–2-butanone–benzene	25	33	6.5 4.6 4.5	0.9	12
Ethanol–chloroform–*n*-hexane	35	36	11.0 11.9 12.3	9.6	26

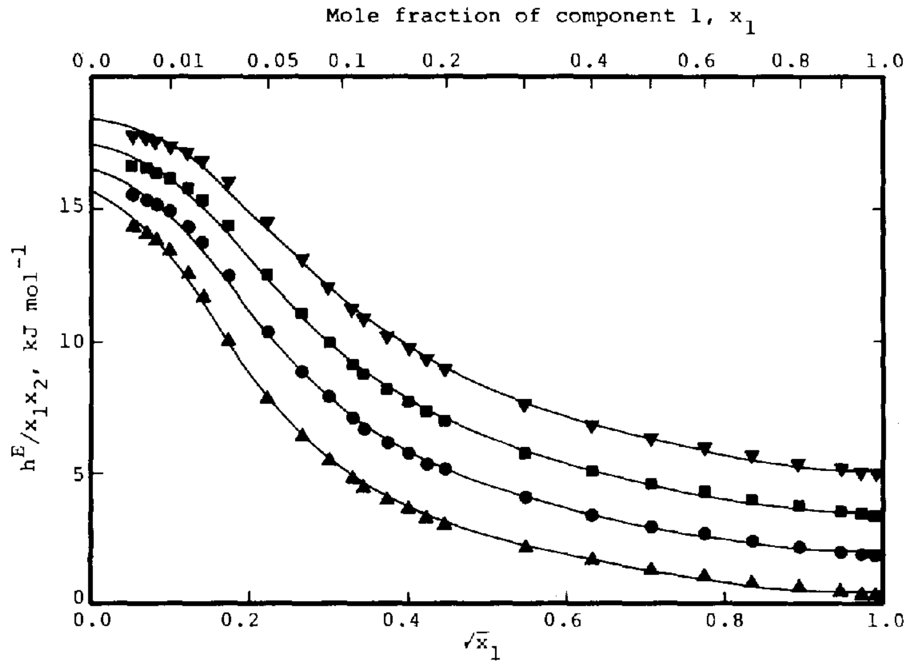


Fig. 4. Molar excess enthalpies of ethanol(1)–*p*-xylene(2). Calculated (———). Experimental (▲, 13.3°C; ●, 25°C; ■, 35°C; ▼, 45°C), data of Stokes and French [2]. Note that the ordinate for the 13.3°C curve is displaced downwards by 1 kJ and those for the 35 and 45°C curves are displaced upwards by 1 and 2 kJ, respectively, to avoid overlap.

TABLE 6

Predicted results for ternary excess enthalpies at 25°C

System	No. of data points	Abs. arith. mean dev. (J mol^{-1})	Ref.
Ethanol–benzene–cyclohexane	18	14.1	27
Ethanol–toluene–cyclohexane	8	26.7	27
Ethanol–*p*-xylene–cyclohexane	59	17.2	23
Ethanol–ethyl acetate–cyclohexane	51	26.8	24

previously described [3]. Figures 1–4 show that the new model reproduces absolute values of activity coefficients and h^E/x_1x_2 for the systems ethanol–cyclohexane and ethanol–*p*-xylene with marked success. In Figs. 1–4 the abscissa $\sqrt{x_1}$ has been used to show the quality of fit in the region up to $x_1 = 0.01$. Table 2 gives the values of constants used in Figs. 1–4 to fit g^E/x_1x_2 or h^E/x_1x_2 data.

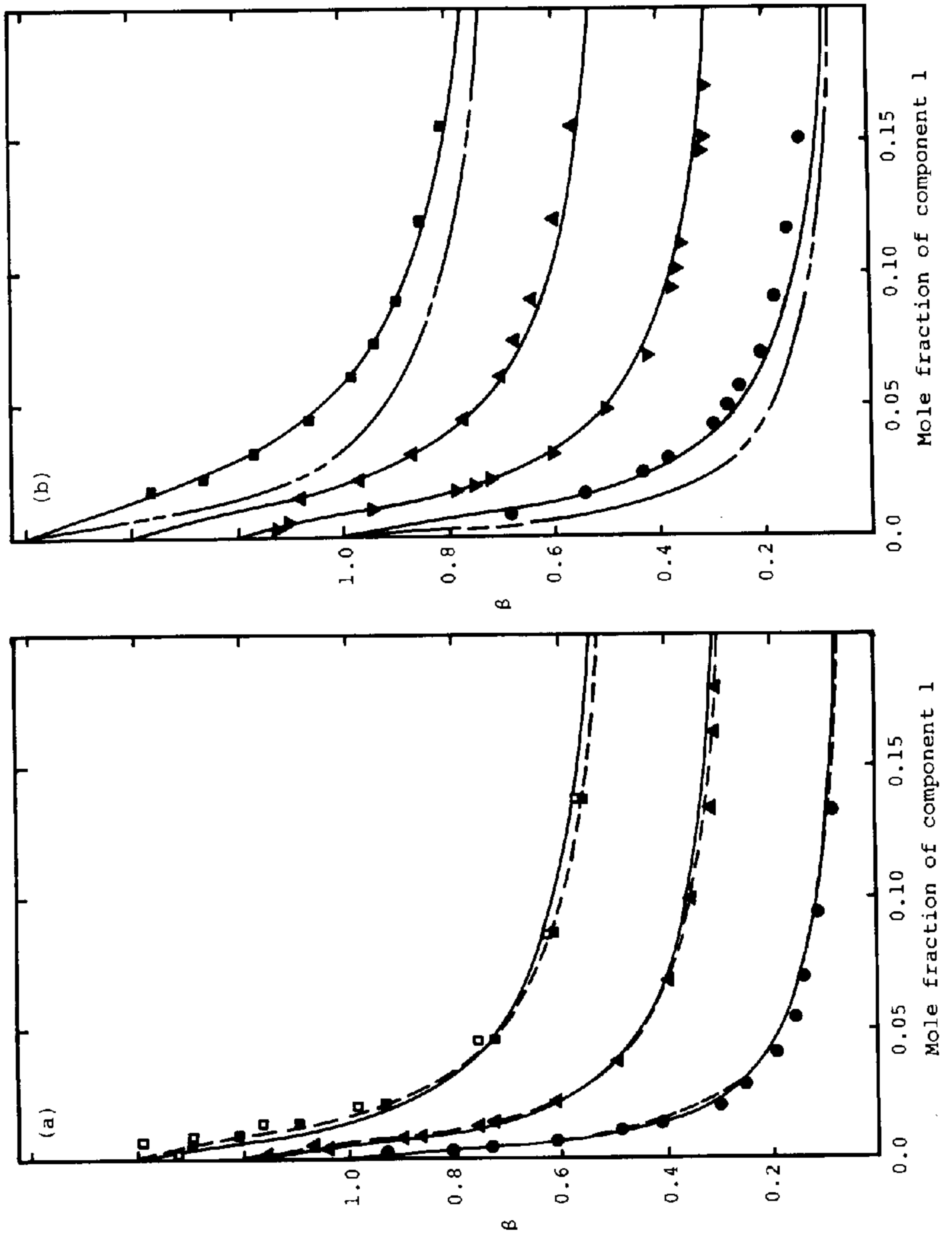
Figure 5 illustrates observed and calculated infrared spectroscopic data for the fraction of free-OH groups of ethanol molecules in two different solvents: (a) cyclohexane; (b) tetrachloromethane. Figure 5b shows clearly that a small but non-zero value of K_{AB} is necessary to obtain a good fit in ethanol(1)–tetrachloromethane(2), although the calculated curve deviates gradually from data at 15°C.

Vapor–liquid equilibrium data reduction was made using the equation

$$\phi_i y_i P = x_i \gamma_i \phi_i^s P_i^s \exp\left[v_i^L (P - P_i^s)/RT\right] \tag{29}$$

where P is the total pressure, P_i^s is the saturated vapor pressure of pure component i, ϕ_i is the fugacity coefficient of component i at P, ϕ_i^s is the fugacity coefficient at P_i^s and T, y_i is the vapor mole fraction of component i, and v_i^L is the molar liquid volume of pure component i. The pure and cross second virial coefficients are estimated by the Hayden–O'Connell method [9] to calculate the fugacity coefficients. The Antoine equation is used to calculate the vapor pressures of pure components [10,11]. The nonrandom-

Fig. 5. Infrared spectroscopic data for fraction of free OH groups for (a) ethanol(1)–cyclohexane(2), and (b) ethanol(1)–tetrachloromethane(2). (a) Calculated (———, this work; - - - - - -, Stokes [1]). Experimental (●, 15°C; ▲, 25°C; □, 35°C), data of Sassa and Katayama [7]. Note that the ordinates for 25 and 35°C curves are displaced upwards by 0.2 and 0.4, respectively, to avoid overlap. ■, Data at 35°C reduced by 10% to adjust for suggested extrapolation error. (b) Calculated (———, $K_{AB} = 1.4$ at 25°C; — - - —, $K_{AB} = 0$). Experimental (●, 15°C; ▲, 25°C; ■, 35°C), data of Sassa and Katayama [7]; ▼, data of Hoffmann [8] at 21.5°C. Note that the ordinates for the 21.5, 25 and 35°C curves are displaced upwards by 0.2, 0.4 and 0.6, respectively, to avoid overlap.


(b)
β
1.0
0.8
0.6
0.4
0.2
0.0
0.05
0.10
0.15
Mole fraction of component 1
(a)
β
1.0
0.8
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0.05
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0.15
Mole fraction of component 1

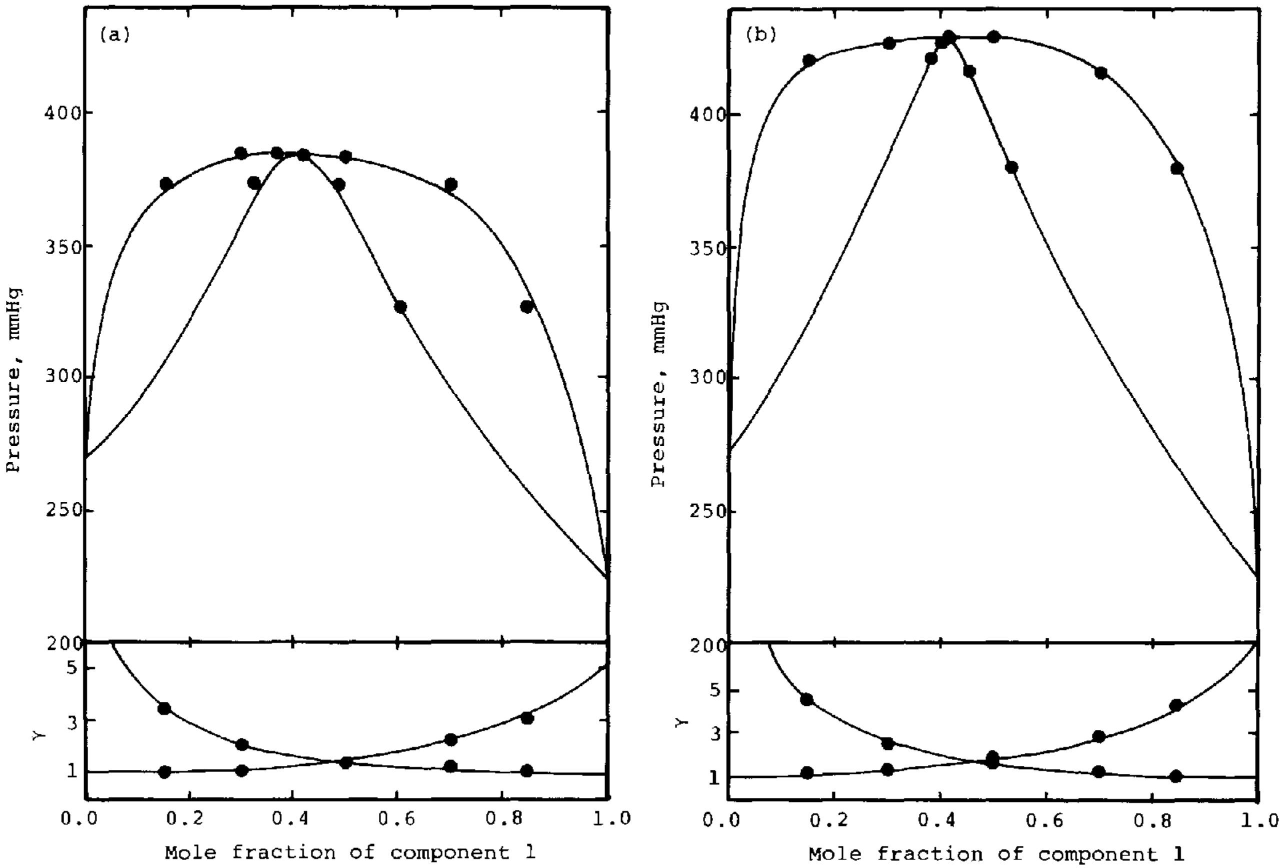

Fig. 6. Vapor–liquid equilibria for (a) ethanol(1)–benzene(2), and (b) ethanol(1)–cyclohexane(2) at 50°C. Calculated (———). Experimental (●) ethanol–benzene, data of Morachevskii and Zharov [13]; ethanol–cyclohexane, data of Zharov et al. [15].

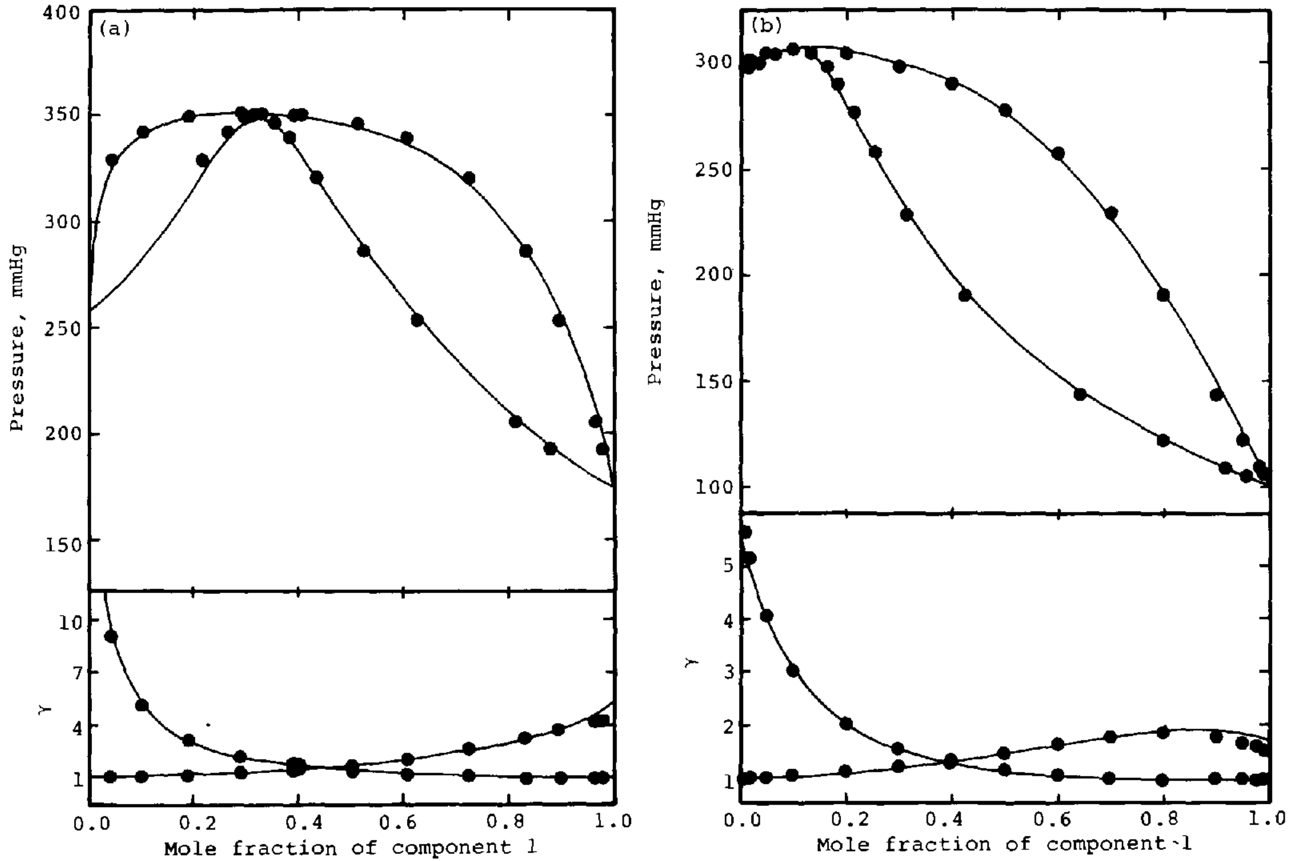

Fig. 7. Vapor–liquid equilibria for (a) ethanol(1)–tetrachloromethane(2) at 45°C, and (b) ethanol(1)–chloroform(2) at 35°C. Calculated (———). Experimental (●) ethanol–tetrachloromethane, data of Barker et al. [17]; ethanol–chloroform, data of Scatchard and Raymond [14].

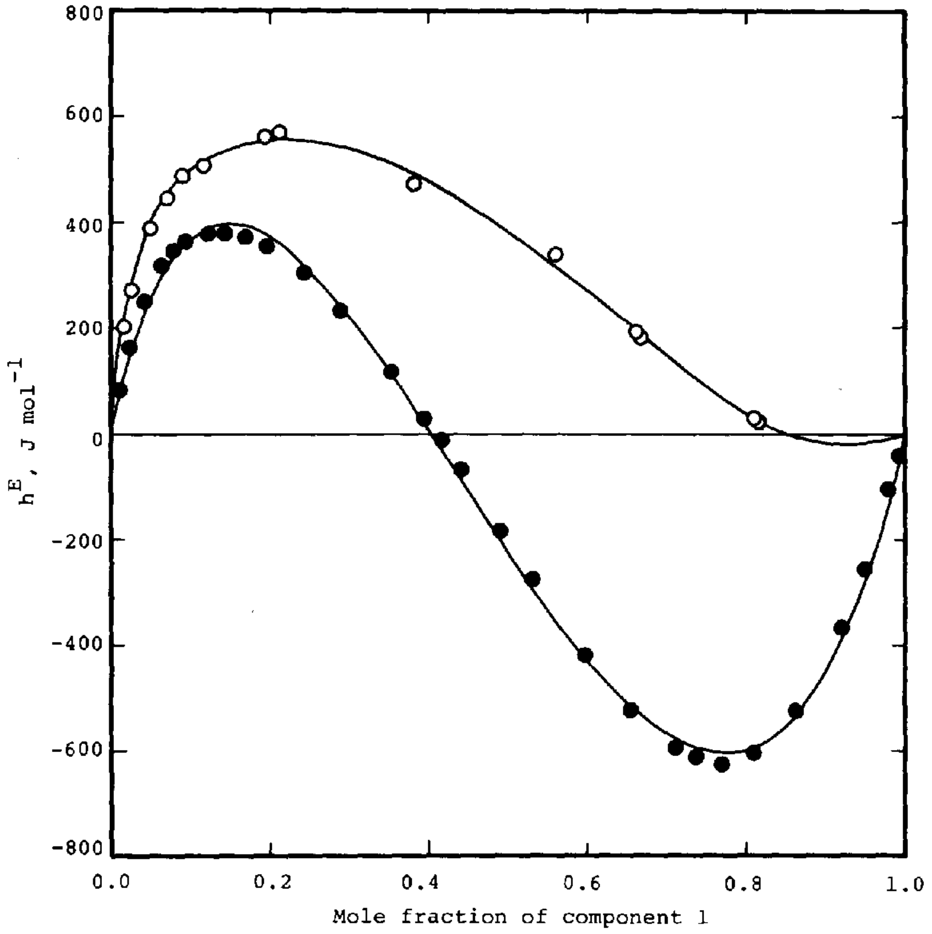

Fig. 8. Molar excess enthalpies for ethanol(1)–tetrachloromethane(2) at 35°C and for ethanol(1)–chloroform(2) at 25°C. Calculated (———). Experimental (○) ethanol–tetrachloromethane, data of Otterstedt and Missen [22]; (●) ethanol–chloroform, data of Nagata et al. [19].

ness parameter of the NRTL equation, $\alpha_{ij}(=\alpha_{ji})$, is taken as 0.3 for all binary systems studied here. Tables 3 and 4 present calculated results for selected binary systems. Figures 6–8 represent typical examples. The results demonstrate that the new model reproduces well the experimental data.

PREDICTION OF TERNARY PROPERTIES FROM BINARY DATA

The model can be extended to predict ternary vapor–liquid equilibria and excess enthalpies by using binary parameters alone. Tables 5 and 6 give predicted results for representative systems. Reasonable agreement is obtained between calculated results and experimental data, indicating that the new model is able to predict the ternary thermodynamic data of solutions of ethanol and nonassociating components.

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